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PATENT SPECIFICATION

DRAWINGS ATTACHED

1,159,551



1,159,551

Date of Application and filing Complete Specification: 9 August, 1966.

No. 35509/66

Application made in United States of America (No. 479523) on 13 August, 1965.

Complete Specification Published: 30 July, 1969.

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Index at Acceptance:—C3 P (7A, 7D2A1, 7D8, 7K8, 7P5, 7P6H, 7P6X, 8A, 8D2B2, 8D5, 8D8, 8K7, 8K8, 8P5, 8P6H, 8P6X, 14A, 14D1A, 14D2F, 14D2J2, 14D3C3, 14D6, 14D8, 14P1X, 14P4C, 14P5, 14P6H, 14P6X); C2 C (KA200, KA22Y, KA220, KA227, KA30Y, KA34Y, KA340, KA366, KA368, KA637, KA71Y, KA799); C3 G (1BX, 1C1, 2B, 2C, 3A4, 3C2).

Int. Cl.:—C 08 f 1/16.

COMPLETE SPECIFICATION

Painting

We, FORD MOTOR COMPANY LIMITED, of 88 Regent Street, London, W.1., a British Company, do hereby declare the invention

The term "ionising radiation" as employed herein means radiation having sufficient energy to remove an electron from a gas atom, forming an ion pair, and hence

ERRATUM

SPECIFICATION NO. 1,159,551

Page 1, For Index at Acceptance C2C only read:— (200, 22Y, 220, 227, 30Y, 34Y, 340, 366, 368, 637, 71Y, 799, KA)

THE PATENT OFFICE,
29th January 1970

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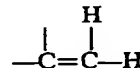
- which comprises applying to the substrate
- 20 a paint binder comprising a film-forming solution in a flow inducing solvent of a vinyl-unsaturated acrylic-urethane-acrylic binder component consisting essentially of an addition product of a diisocyanate and a
 - 25 C₆ to C₁₂ monohydroxylated acrylic monomer in an excess of said monomer, the said addition product having a molecular weight below 900, and irradiating the film with ionising radiation.
 - 30 In this application the term "paint" is meant to include finely ground pigment and/or filler in the binder, the binder without pigment and/or filler or having very little of the same, which can be tinted if desired,
 - 35 and other surface coating compositions containing the binder which might be considered to be broadly analogous to enamel, varnish, or lacquer bases. Thus, the binder which is ultimately converted to a durable
 - 40 film resistant to conventional curing, can be all or virtually all that is used to form the film, or it can be a vehicle for pigmentary and/or mineral filler material.

[Price

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piece where the adjustment is made by air. Adjustment is made for the relative resistance of the intervening gas which is preferably an oxygen-free, inert gas such as nitrogen or helium. It is, however, within the scope of this invention to effect polymerization using either that which is conventionally termed "high energy particle radiation" or "ionizing electromagnetic radiation".

The term "vinyl" as employed herein refers to any organic polymer or monomer having a



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terminal grouping.

The term "acrylic monomer" as used herein means an alpha-beta monounsaturated, monocarboxylic acid or esters thereof and includes, but not by way of limitation, acrylic acid, alkacrylic acids, e.g. methacrylic acid, monohydric and polyhydric alcohol esters of acrylic acid and alkacrylic acids, other oxygenated derivatives of acrylic

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SEE DRAWING SHEET FOR FIGURE

PATENT SPECIFICATION

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Int. Cl.:—C 08 f 1/16.

COMPLETE SPECIFICATION

Painting

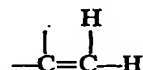
We, FORD MOTOR COMPANY LIMITED, of 88 Regent Street, London, W.1., a British Company, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the art of coating and is primarily concerned with method and means for providing articles of manufacture, particularly wood and/or metal surfaces thereof, with decorative and abrasion resistant coatings, including improved paints for such purpose, their preparation, application to a substrate and polymerisation thereon. More particularly, this invention provides a method of coating a substrate which comprises applying to the substrate a paint binder comprising a film-forming solution in a flow inducing solvent of a vinyl-unsaturated acrylic-urethane-acrylic binder component consisting essentially of an addition product of a diisocyanate and a C₃ to C₈ monohydroxylated acrylic monomer in an excess of said monomer, the said addition product having a molecular weight below 900, and irradiating the film with ionising radiation.

In this application the term "paint" is meant to include finely ground pigment and/or filler in the binder, the binder without pigment and/or filler or having very little of the same, which can be tinted if desired, and other surface coating compositions containing the binder which might be considered to be broadly analogous to enamel, varnish, or lacquer bases. Thus, the binder which is ultimately converted to a durable film resistant to conventional curing, can be all or virtually all that is used to form the film, or it can be a vehicle for pigmentary and/or mineral filler material.

The term "ionising radiation" as employed herein means radiation having sufficient energy to remove an electron from a gas atom, forming an ion pair, and hence radiation with energy of, or equivalent to, about 5,000 electron volts is operative for effecting polymerisation of the paint films herein disclosed. The preferred method of curing films of the instant paint binders upon the substrates to which they have been applied is by subjecting such films to a beam of polymerisation effecting electrons which at its source of emission is within the range of, or equivalent to 150,000 to 450,000 electron volts. In this method of curing, it is preferred to employ a minimum of 25,000 electron volts per inch of distance between the radiation emitter and the work-piece where the intervening space is occupied by air. Adjustment is made for the relative resistance of the intervening gas which is preferably an oxygen-free, inert gas such as nitrogen or helium. It is, however, within the scope of this invention to effect polymerization using either that which is conventionally termed "high energy particle radiation" or "ionizing electromagnetic radiation".

The term "vinyl" as employed herein refers to any organic polymer or monomer having a



terminal grouping.

The term "acrylic monomer" as used herein means an alpha-beta monounsaturated, monocarboxylic acid or esters thereof and includes, but not by way of limitation, acrylic acid, alkacrylic acids, e.g. methacrylic acid, monohydric and polyhydric alcohol esters of acrylic acid and alkacrylic acids, other oxygenated derivatives of acrylic

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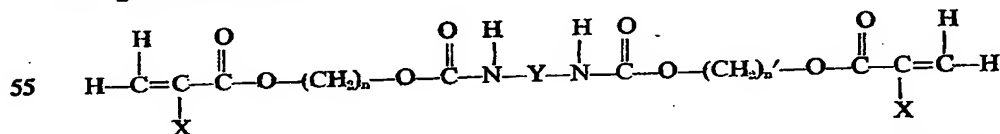
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acid and alkacrylic acid, e.g. glycidyl methacrylate and 2-hydroxyethyl methacrylate, and in special situations halogenated derivatives of the same, e.g. chloroacrylic acid and esters thereof.

The accompanying drawing illustrates the preparation of the acrylic-urethane-acrylic addition product by adding a diisocyanate monomer to the monohydroxylated acrylic monomer incrementally with continuous stirring. The acrylic monomer may be in solution with an inert solvent and the reaction mixture is preferably maintained in an inert atmosphere, e.g. nitrogen, while the reaction is carried out. The addition should be at a rate such that the resulting exotherm preferably does not exceed 32°C. The resultant reaction is between the —NCO groups of the diisocyanate and the —OH group of the vinyl monomers leaving the vinyl unsaturation unreacted. The reaction is exothermic and self-generating. With certain diisocyanates, e.g. 2,4-diisocyanate, one of the two isocyanate groups reacts with a hydroxyl group at a much greater rate than does its companion.

Among the diisocyanates which may be used are 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate, 1,5-naphthalene diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, hexamethylene diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 4,4'-diphenylmethane diisocyanate, 3,3'-dimethylbiphenylene diisocyanate, 4,4'-biphenylene diisocyanate, 3,3'-dimethoxy-4,4'-dimethyl-4,4'-biphenylene diisocyanate, durene diisocyanate, 1-phenoxy-2,4-phenylene diisocyanate and 1-tert-butyl-2,4-phenylene diisocyanate. Many of the foregoing while operable are prohibitively expensive for use in any large scale coating operation. In special applications it may be advantageous to utilise one of the halogenated diisocyanates, e.g. 1-chloro-2,4-phenylene diisocyanate. In one preferred embodiment at least as many diisocyanate molecules are charged as there are reactive hydroxyl groups on the starting resin. The addition product may, for example, have the formula:



in which X is hydrogen or a methyl group, n is an integer from 1 to 8, n' is an integer from 1 to 8 and Y is a C₆ to C₁₀ divalent hydrocarbon radical.

The resultant product has a molecular weight of less than 900, preferably below 600, and may be applied to a substrate and polymerised thereon by ionising radiation without employing other radiation polymerisable material. It may be admixed with vinyl monomers, which form the solvent of the paint binder, e.g. acrylic monomers, vinyl hydrocarbon monomers and mixtures of the same, and copolymerised upon the substrate to be coated. Preferably, the product is employed as a urethane-modifying agent in a radiation curable, film-forming solution of an olefinically unsaturated resin having a molecular weight in excess of 1,000 suitably in excess of 2,000 and suitably below 50,000, and vinyl monomers as afore-described. Such resins have 0.5 to 3, preferably 1 to 2 olefinic unsaturation units per 1,000 units molecular weight and include polyester resins, silicone-modified polyester resins, acrylic resins and modified-acrylic resins. The molecular weight of these resins will vary somewhat with type but advantageously these are in the range of 2,000 to 50,000, preferably 2,000 to 25,000. The compositions containing the addition product and organic resin form the subject-

matter of our copending Application No. 90 5426/69 (Serial No. 1,159,552).

The term "acrylic resin" as employed herein means a resin formed exclusively from acrylic monomers. The term "modified-acrylic resin" as employed herein means a resin formed from a major amount of acrylic monomers and a minor amount of non-acrylic monomers.

The binder is preferably applied to the substrate and cured thereon as a continuous film of substantially even depth, preferably a depth in the range of 0.1 to 4.0 mils depending upon the substrate and the intended end use of the coated product. The paint binder may be applied to the substrate by conventional spray techniques in which case it has a viscosity in the range of 5 to 50, preferably 10 to 35, seconds (Ford Cup), or by brushing, roll coating, flow coating, or by the method commonly termed the silk screen process with appropriate adjustment in viscosity. The film-forming material should have a viscosity low enough to permit rapid application to the substrate in substantially even depth and high enough so that a 1 mil (.001") film will hold upon a vertical surface without sagging. The viscosity of the binder is adjusted by varying the molecular weight of the resin or resins and/or by varying the relative concentrations of the resin component, the acrylic-

urethane-acrylic polymer and the vinyl monomers, and/or by varying the relative concentrations of dissimilar monomers within the monomer component. The binder is preferably applied to the substrate essentially free of non-polymerisable organic solvents and/or diluents.

The films formed from the preferred embodiments of the paints of this invention are cured at relatively low temperatures, e.g. between room temperature (20 to 25°C) and the temperature at which significant

vapourisation of its most volatile component is initiated, ordinarily between 20° and 70°C. The radiation energy is applied at dose rates of 0.1 to 100 Mrad per second upon a preferably moving workpiece with the coating receiving a total dose in the range of 0.1 to 100, preferably 1 to 25, Mrad. Such films are converted by the electron beam into tenaciously bound, wear and weather resistant, coatings which meet the following specifications:

25 SUBSTRATE APPLICABILITY

TYPE OF EXPOSURE

REQUIREMENTS OF TEST

wood or metal room temperature water soak

withstand 240 hours immersion in water at 20 to 25°C (68 to 77°F) without significant loss of gloss or film integrity, i.e. without blistering, checking, cracking or peeling

wood cyclic boiling and baking

withstand 25 cycles — each 4 hours immersion in boiling water followed by 15 hours drying at 62 to 63°C (about 144 to 146°F) — without significant loss of gloss or film integrity

metal elongation

withstand 25% elongation without rupture — 1 to 2 mil coating — $\frac{1}{8}$ " mandrel

wood or metal ultraviolet

withstand 2,000 hours exposure in Standard Atlas Ultraviolet Carbon Arc Weatherometer test without significant chalking and without loss of gloss or film integrity. (The word "Atlas" is a Registered Trade Mark).

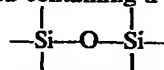
The preferred polyester resins are prepared from an acyclic dibasic acid or anhydride, e.g. maleic anhydride or succinic acid, an aliphatic, cyclic, dibasic acid or anhydride, e.g. tetrahydrophthalic anhydride or 1,4-cyclohexane-dicarboxylic acid, and a branched chain polyhydric alcohol, e.g. neopentyl glycol. In one embodiment all or a portion of the branched chain polyhydric alcohol, is replaced with a straight chain polyhydric alcohol, e.g. 1,4-butanediol. A cyclic aromatic dibasic acid or anhydride, e.g. phthalic anhydride, may be used by aliphatic cyclic acids are preferred.

The alkyd type polyester resins employed herein have molecular weights in the range of 1,000 to 10,000, preferably above about 2,500, and an acid number in the range of 5 to 50, preferably below 20.

In a second embodiment the resin is prepared by the copolymerisation of acrylic monomers. Insofar as acrylate and methacrylate monomers are used in the polymerisation, the acrylic resins also have a plurality of ester linkages. A suitable resin is a copolymer of the following acrylic monomers in the following relative proportions:

- (a) methyl methacrylate 2 to 3
- (b) ethyl acrylate 4 to 6
- (c) glycidyl methacrylate 1.25 to 2.25
- (d) methacrylic acid 1.25 to 2.25

In a third embodiment the resin is a silicone-modified polyester resin. The preferred silicone-modified resins employed herein are polyester type resins with the aforementioned degree of unsaturation and of which at least 10, advantageously 15 to 50 or 55 wt.%, and preferably 20 to 40 wt.%, is derived from a siloxane having prior to its incorporation a reactive hydroxyl or hydrocarbonoxy group bonded to at least two of its silicon atoms. Suitably the resin is at least partly derived from a cyclic siloxane which may suitably have from 13 to 18 silicon atoms per molecule. In the case of resins derived at least partly from an acrylic siloxane this suitably has from 3 to 12 silicon atoms per molecule. The term "siloxane" as employed herein refers to a compound containing a



linkage, with the remaining valences being satisfied by a hydrocarbon radical, a hydrocarbonoxy group, hydrogen, a hydroxyl

100

group, or an oxygen atom which interconnects the silicon atom proving such valence with another silicon atom. A variety of methods are known to the art for preparing siloxanes. These include controlled hydrolysis of silanes, polymerisation of a lower molecular weight siloxane in the presence of an alkoxysilane and reacting silicon tetrachloride with an alcohol. The preparation of siloxanes and their incorporation into organic resins is disclosed in U.S. Patents 3,154,597; 3,074,904; 3,044,980; 3,044,979; 3,015,637; 2,996,479; 2,973,287; 2,937,230; 2,090,549; and 2,877,202.

In one preferred embodiment a silicone-modified polyester type resin is prepared by first reacting the acyclic siloxane with a polyhydric alcohol, preferably a branched chain polyhydric alcohol such as neopentyl glycol, and subsequently reacting the first product with an acyclic, alpha-beta unsaturated, dicarboxylic acid or the anhydride thereof, e.g. maleic anhydride, and a cyclic, aliphatic, dicarboxylic acid or its anhydride, e.g. tetrahydrophthalic anhydride.

In another embodiment the polyester is formed first by reacting the aforementioned polyhydric alcohol, the acyclic, alpha-beta unsaturated, dicarboxylic acid or anhydride and the cyclic, aliphatic, dicarboxylic acid or anhydride either with or without a straight chain polyhydric alcohol, e.g. a propane or butane diol, and subsequently reacting this product with the siloxane.

In another embodiment an unsaturated polyester is formed as in the previously described embodiments or a saturated type polyester if formed by substituting a saturated acyclic dibasic acid such as succinic acid for the maleic anhydride and after reaction of the siloxane with monomer or polymer as the case may be, the remaining hydroxyl or hydrocarbonoxy groups on the siloxane are reacted with suitably unsaturated hydroxylated monomers or low molecular weight esters, e.g. the reaction product of maleic anhydride and a polyhydric alcohol, to provide the desired unsaturation for polymerization.

In another embodiment a hydroxylated vinyl resin is prepared by reacting the vinyl monomers, e.g. acrylic acid, methacrylic acid and esters thereof, at least one of which is a hydroxylated monomer such as 2-hydroxyethyl methacrylate, a portion of the hydroxyl or hydrocarbonoxy groups of the siloxane are reacted with the hydroxyl groups of the resin and the remainder are subsequently reacted with a hydroxylated unsaturated compound.

The paint binder solution advantageously contains 1 to 20, advantageously 2 to 15, preferably 2 to 10, percent of the acrylic-urethane-acrylic addition product and 80 to 98 percent of a film-forming solution of

an olefinically unsaturated resin having an average molecular weight in excess of 1,000 in vinyl monomers, said solution containing 30 to 70, preferably 40 to 60, percent of said resin and 30 to 70, preferably 40 to 60, percent of unpolymerized vinyl monomers. In a preferred embodiment the vinyl monomers of the paint binder are a mixture of 30 to 70, preferably 40 to 60, and more preferably 45 to 55, percent acrylic monomers with the balance non-acrylic vinyl monomers. For example, increased weathering resistance can be obtained by increased concentration of an acrylic monomer such as methyl methacrylate while a lowering of the requisite radiation dosage can be obtained by increasing the concentration of a vinyl hydrocarbon monomer such as styrene and the respective quantities of such monomers may be adjusted to fit the individual need.

This invention will be more easily understood from the following illustrative examples:

EXAMPLE I

A low molecular weight acrylic-urethane-acrylic binder component is prepared from the following materials:

	Mols	Grams
2-hydroxyethyl methacrylate	0.3388	44.08
tolyene diisocyanate, monomer mixture ⁽¹⁾	0.1540	27.00

(1) 80% 2,4-tolyene diisocyanate
20% 2,6-tolyene diisocyanate

The diisocyanate is added dropwise to the methacrylate while stirring in a nitrogen gas atmosphere: A rate of addition is maintained so that the exotherm does not exceed 32°C. Stirring is continued for an hour after addition is completed, and the mixture allowed to stand for 16 hours at room temperature.

The reaction product is divided into three parts. A 50% solution is made of the first part in methyl ethyl ketone. A 50% solution of the second part is made in even parts of styrene and methyl methacrylate. A 50% solution of the third part is made in methyl methacrylate. Films of each of these are sprayed upon 3" x 5" phosphated steel panels. Flash time is allowed to remove a substantial amount of the methyl ethyl ketone.

The panels are irradiated using an electron beam under the following conditions:

Potential	295 KV
Current	1 milliampere
Distance, emitter to workpiece	10 inches
Line speed	2
Passes	10 Mrad
Total dosage	

The coatings exhibit a Sward Hardness of about 54.

EXAMPLE 2

A silicone-modified polyester, paint binder resin is prepared in the following manner:

To a reaction vessel are charged 1330 lbs. of neopentyl glycol and 1080 lbs. of a commercially available methoxylated partial hydrolysate of monophenyl and phenyl-methyl silanes consisting essentially of dimethyltriphenyltrimethoxytrisiloxane (Dow Corning — Sylkyd 50) (the word "Dow" is a Registered Trade Mark, as is the word "Sylkyd") and have the following typical properties:

Average molecular weight	470
Combining weight	155
Specific gravity at 77°F	1.105
Viscosity at 77°F, centistokes	13

The charge is heated to about 345°F (174°C) until about 215 lbs. methanol are removed overhead. The charge is cooled to about 250°F (121°C) after which there is added 196 lbs. maleic anhydride, 964 lbs. tetrahydrophthalic anhydride, 2.2 lbs. dibutyl tin oxide and 150 lbs. xylene. The temperature of the charge is raised slowly to about 420°F (215°C) and this temperature is maintained until the resulting resin has an acid number of 10. A vacuum is used to remove the xylene and 61 lbs. hydroquinone are charged and the charge is cooled to 200°F and dumped into a mixing tank with 780 lbs. styrene.

A white mill base is then prepared by mixing 3050 lbs. of TiO₂, 1805 lbs. of resin, prepared as in the preceding paragraph, 146 lbs. of styrene, 507 lbs. of methyl methacrylate, and 20 lbs. of Bakers M.P.A., a wax-like, high molecular weight, castor oil derivative to facilitate the grinding through viscosity adjustment and assist in retention of pigment dispersion in the grind, and passing the foregoing mixture through a conventional sand grinder.

This mill base is further diluted with styrene and methyl methacrylate and 90 wt. % of this solution is admixed with 10 wt. % of the acrylic-urethane-acrylic addition product of Example 1 providing a paint comprising about 36% resin, about 27% styrene, about 27% methyl methacrylate and about 10% of the acrylic-urethane-acrylic addition product. A film of the resulting paint is sprayed upon wood and metal panels and irradiated by an electron beam under the following conditions:

Potential	295 KV
Current	1 milliampere
Distance, workpiece to emitter	10 inches
Atmosphere	helium
Line speed	4.8 cm/sec.
Total dose	1.67 Mrad

EXAMPLE 4

A silicone-modified polyester, paint binder resin is prepared in the following manner:

To a reaction vessel are charged 70 lbs. of neopentyl glycol, 10 lbs. of xylene, and 35 lbs. of a commercially available (Dow Corning Z-6018) hydroxy-functional, cyclic, polysiloxane having the following properties:

Hydroxy content, Dean Stark		
percent condensible	5.5	
percent free	0.5	
Average molecular weight	1600	80
Combining Weight	400	
Refractive index	1.531 to 1.539	
Softening point, Durran's Mercury Method, degrees F.	200	85

At 60% Solids in xylene		
Specific gravity at 77°F	1.075	
Viscosity at 77°F, centipoises	33	90
Gardner-Holdt	A-1	

The charge is heated to about 345°F (174°C) for 2½ hours, after which there is added 13.7 lbs. maleic anhydride, 54.2 lbs. of tetrahydrophthalic anhydride and 100 grams of dibutyl tin oxide. The temperature of the charge is raised slowly to about 430°F (221°C) and this temperature is maintained until the resulting resin has an acid number of about 10. Some of the xylene and water of reaction are removed during the cook and the excess is then removed by vacuum. To the charge is added 12.5 grams hydroquinone and the charge is cooled to 180°F (82.5°C) and diluted with 40 lbs. of styrene.

A white mill base is then prepared by mixing 3050 lbs. of TiO₂, 1805 lbs. of resin, prepared as in the preceding paragraph, 146 lbs. of styrene, 507 lbs. of methyl methacrylate, and 20 lbs. of Bakers M.P.A., a wax-like, high molecular weight, castor oil derivative to facilitate the grinding through viscosity adjustment and assist in retention of pigment dispersion in the grind, and passing the foregoing mixture through a conventional sand grinder.

The mill base is further diluted with styrene and methyl methacrylate and 95 wt. % of this solution is admixed with 5 wt. % of the acrylic-urethane-acrylic addition product of Example 1 providing a paint comprising about 38% resin, about 28.5% styrene, about 28.5% methyl methacrylate and 5% of the acrylic-urethane-acrylic addition product. A film of the resulting paint is sprayed upon wood and metal panels and irradiated by an electron beam under the following conditions:

130

Potential	295 KV
Current	1 milliampere
Distance, emitter to workpiece	10 inches
Line speed	1.6 cm/sec.
Passes	2
Total dosage	10 Mrad.

	Mols	Grams
(a) Methyl methacrylate	2.6	260.0
(b) Ethyl acrylate	5.0	500.0
(c) Glycidyl methacrylate	1.7	240.0
(d) Methylacrylic acid	1.7	146.5
(e) Xylene	1000 ml.	
(f) Benzoyl peroxide		10.0
(g) Hydroquinone		0.2

EXAMPLE 3

- 10 The procedure of Example 2 is repeated except that the amount of acrylic-urethane-acrylic polymer employed is changed from 10 wt. % to 2, 8, 12, 15 and 20 wt. % in separate applications.

EXAMPLE 5

- 15 The procedure of Example 2 is repeated except for the difference that the neopentyl glycol, the maleic anhydride and the tetrahydrophthalic anhydride are reacted together and the product is subsequently reacted with the siloxane until clear at 350°F (176°C) maximum.

EXAMPLE 6

- 25 A resin is prepared from the following monomers:

	Mols	Grams
Maleic anhydride	3.6	353.0
30 Tetrahydrophthalic anhydride	6.4	973.8
Neopentyl glycol	14.0	1458.1

- A fusion cook of the tetrahydrophthalic anhydride and neopentyl glycol is carried out over a 23-hour period. Water comes over at 165°C and a maximum temperature of 180°C is recorded. The resulting resin has an acid number of below 15 and is cooled to room temperature after which the maleic anhydride is added with 1.39 grams hydroquinone and 300 cc xylene. The charge is heated to an acid number of 10 with water coming over at about 140°C and a maximum temperature of 180° recorded.

- 45 A paint binder is prepared using 4 parts by weight of the acrylic-urethane-acrylic addition product of Example 1, 48 parts by weight of the above resin, 24 parts by weight styrene and 24 parts by weight of methyl methacrylate. The binder is sprayed upon wood and metal panels and irradiated as in the previous examples.

- 55 A paint binder is prepared using 2 parts by weight of the acrylic-urethane-acrylic addition product of Example 1, 25 parts by weight of the above polyester resin, 10 parts by weight of styrene, 10 parts methyl methacrylate and 5 parts by weight ethylene glycol dimethacrylate. The binder is sprayed upon wood and metal panels and irradiated as in the preceding examples.

EXAMPLE 7

- 65 An acrylic paint binder resin is prepared from the following monomers:

The xylene is heated to 130°C under a 75 nitrogen blanket and stirred continuously. The monomers (a), (b) and (c), the reaction initiator (f) and the hydroquinone (g) are added to the xylene. The monomers (a), (b) and (c) are added separately and incrementally over a period of 3 hours. The charge is heated at 130°—133°C for about 3 hours. The charge is cooled to about 50°C.

The methacrylic acid (d) is added to the charge and the temperature is raised to 85 138°C gradually over a period of about 1.5 hours. This temperature is maintained for about 1 hour and the xylene is removed.

A paint binder is prepared by admixing the acrylic polymer thus formed (45 parts by weight), styrene (15 parts by weight), methyl methacrylate (35 parts by weight) and the acrylic-urethane-acrylic product of Example 1 (5 parts by weight). A film of this binder is sprayed upon wood and metal panels and irradiated by an electron beam as in the preceding example.

EXAMPLE 8

The procedure of Example 7 is repeated except that 0.6 mol of methyl methacrylate in the resin is replaced with 0.6 mol of styrene and hexamethylene diisocyanate is substituted for the tolylene diisocyanate.

EXAMPLE 9

The procedure of Example 2 is repeated with the potential of the electron beam adjusted to about 175,000 electron volts. The exposure is controlled to provide a total dose equivalent to that of Example 2.

EXAMPLE 10

The procedure of Example 2 is repeated with the potential of the electron beam adjusted to about 400,000 electron volts. The exposure is controlled to provide a total dose equivalent to that of Example 2.

EXAMPLE 11

The procedure of Example 7 is repeated varying the concentrations of the ingredients of the resin-monomer solution prior to a 5% addition of the acrylic-urethane-acrylic polymer of Example 1.

The concentrations employed are as follows:

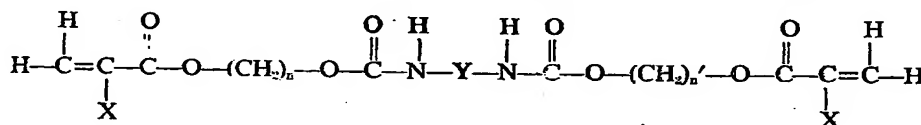
Resin %	Styrene %	Methyl Methacrylate %	
60	20	20	
50	20	30	
50	30	20	
40	30	30	130

The acrylic-urethane-acrylic modifier is then added and the several paint binders are sprayed upon wood and metal panels and irradiated as in the preceding examples.

- 5 The abbreviation Mrad as employed herein means 1,000,000 Rad. The term "Rad" as employed herein means that dose of radiation which results in the absorption of 100 ergs of energy per gram of absorber, e.g. coating film. The electron emitting means may be a linear electron accelerator capable of producing a direct current potential in the range hereinbefore set forth. In such a device electrons are ordinarily emitted from a hot filament and accelerated through a uniform voltage gradient. The electron beam, which may be about $\frac{1}{8}$ " in diameter at this point, is then scanned in one direction to make a fan-shaped beam and then passed through a metal window, e.g. a magnesium-thorium alloy of about 0.003" thickness.

WHAT WE CLAIM IS:—

- 25 1. A method of coating a substrate which comprises applying to the substrate a paint binder polymerisable by means of ionising radiation and comprising a film-forming solution in a flow-inducing solvent of a vinyl-unsaturated acrylic-urethane-



wherein X is hydrogen or a methyl radical, n is a positive integer of 1 to 8, n' is a positive integer of 1 to 8, and Y is a C₆ to C₁₆ divalent hydrocarbon radical.

- 70 8. A method as claimed in any of claims 1 to 7 in which the addition product has a molecular weight less than 600.
 9. A method as claimed in any of claims 1 to 8 in which the paint binder solvent consists of vinyl monomers.
 10. A method as claimed in claim 9 in which the solvent is a mixture of acrylic and vinyl hydrocarbon monomers.
 11. A method as claimed in claim 10 in which the solvent comprises 40% to 60% by weight acrylic monomers.
 12. A method as claimed in claim 10 or 11 in which the solvent is a mixture of methyl methacrylate and styrene.
 85 13. A method as claimed in any of claims 1 to 12 in which the paint binder further comprises dissolved in the solvent an organic resin having a molecular weight in excess of 1000 and containing 0.5 to 3 olefinic unsaturation units per 1000 units molecular weight, the resin being copolymerisable with the addition product by ionising radiation.

acrylic binder component consisting essentially of an addition product of a diisocyanate and C₆ to C₁₆ monohydroxy acrylic monomer, the said addition product having a molecular weight below 900, and irradiating the film with ionising radiation.

2. A method as claimed in claim 1 in which the binder component consists essentially of an addition product formed by reacting the said diisocyanate with an excess of the acrylic monomer.

3. A method as claimed in claim 1 or 2 in which the addition product has at least 2 urethane groups and at least 2 vinyl unsaturation units per molecule.

4. A method as claimed in claim 1, 2 or 3 in which the binder component consists essentially of an addition product of 1 molecule of diisocyanate monomer and 2 molecules of C₆ to C₁₆ monohydroxy acrylic monomer.

5. A method as claimed in claim 4 in which the diisocyanate is tolylene diisocyanate.

6. A method as claimed in claim 4 or 5 in which the acrylic monomer is 2-hydroxyethyl methacrylate.

7. A method as claimed in any one of claims 1 to 6 in which the addition product is represented by the formula:

14. A method as claimed in claim 13 in which the resin has a molecular weight in excess of 2000.

15. A method as claimed in claim 13 or 14 in which the resin has a molecular weight below 50,000.

16. A method as claimed in claim 13, 14 or 15 in which the resin has about 1 to 2 olefinic unsaturation units per 1000 units molecular weight.

17. A method as claimed in any of claims 13 to 16 in which the resin is a polyester resin.

18. A method as claimed in any of claims 13 to 16 in which the resin is a silicone-modified resin.

19. A method as claimed in any of claims 13 to 16 in which the resin is a silicone-modified polyester resin.

20. A method as claimed in claim 18 or 19 in which at least 10% of the weight of the resin is derived from a siloxane.

21. A method as claimed in claim 18 or 19 in which 15 to 55% of the weight of the resin is derived from a siloxane.

22. A method as claimed in any of claims 18 to 21 in which the resin is at least partly derived from a cyclic siloxane.

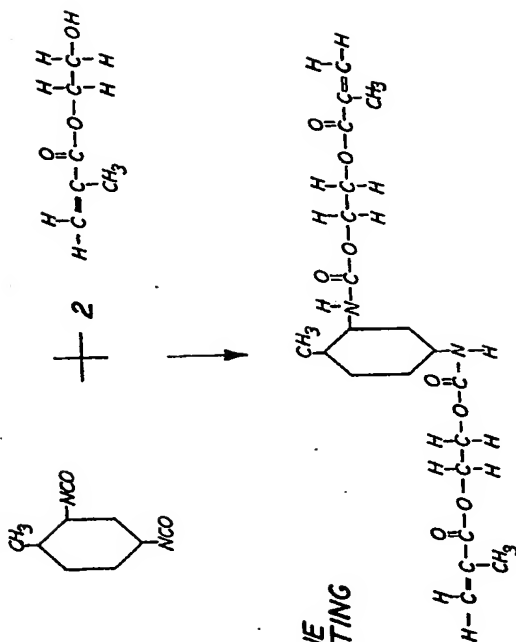
23. A method as claimed in any of claims 18 to 21 in which the resin is derived at least partly from an acyclic siloxane.
24. A method as claimed in any of 5 claims 18 to 21 in which the resin is at least partly derived from a cyclic siloxane having 13 to 18 silicon atoms per molecule.
25. A method as claimed in any of 10 claims 14 to 17 in which the resin is at least partly derived from an acyclic siloxane having 3 to 12 silicon atoms per molecule.
26. A method as claimed in claim 17 or 15 18 or in any of claims 20 to 25 as appended to claim 19, in which the polyester resin is a copolymer of an acyclic alpha-beta unsaturated dicarboxylic acid or anhydride, a cyclic aliphatic dicarboxylic acid or anhydride, and a polyhydric alcohol.
27. A method as claimed in claim 26 in which the polyester resin is a copolymer of maleic anhydride, tetrahydrophthalic anhydride, and the polyhydric alcohol.
- 25 28. A method as claimed in claim 26 or 27 in which the polyhydric alcohol is a branched chain polyhydric alcohol.
29. A method as claimed in claim 26 or 27 in which the polyhydric alcohol is 30 neopentyl glycol.
30. A method as claimed in any of claims 13 to 16 in which the resin is an acrylic or modified acrylic resin.
31. A method as claimed in claim 30 25 in which the resin is a copolymer of methyl methacrylate, ethyl acrylate, glycidyl acrylate, and methacrylic acid.
32. A method as claimed in claim 30 in which the resin is a copolymer of the following acrylic monomers in the follow- 40 ing relative molar concentrations:
- | | |
|---------------------------|------------------|
| (a) methyl methacrylate | 2 to 3 |
| (b) ethyl acrylate | 4 to 6 |
| (c) glycidyl methacrylate | 1.25 to 2.25 |
| (d) methacrylic acid | 1.25 to 2.25. 45 |
33. A method as claimed in any of claims 13 to 32 in which the paint binder contains by weight, 2% to 20% of the addition product and 98% to 80% of the solvent and resin, the relative proportions of 50 solvent and resin by weight being in the range of 30% to 70% of solvent and 70% to 30% resin.
34. A method as claimed in claim 33 in which the relative proportions of solvent 55 and resin by weight are in the range of 40% to 60% solvent and 60% to 40% resin.
35. A method as claimed in any one of the preceding claims in which the film is applied with an average depth in the range 60 of 0.1 to 4 mils.
36. A method as claimed in any one of the preceding claims in which the ionising radiation consists of electrons.
37. A method as claimed in claim 36 in 65 which the electrons have energies in the range of 150,000 to 450,000 electron volts.
38. A method of coating a surface, substantially as described in any one of the foregoing Examples. 70

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